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LOCALIZED MAGNETIC MOMENTS IN METALS

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A simple model is used to obtain information about localized magnetic moments in metals from Mössbauer (or nuclear magnetic resonance) experiments. The formulation emphasizes the explicit dependence of the hyperfine field on the spin S′ of the Fe atom and shows why the temperature dependence of the hyperfine field follows a Brillouin function of the total localized spin S (with $S \neq S'$). The moment of Fe atoms in dilute concentrations of Pd, Rh, and Mo are determined and the apparent contradiction between Mössbauer and susceptibility measurements for Rh and Mo is discussed.

Large magnetic moments associated with Fe atoms dissolved in non-magnetic 4d metals have been extensively studied by means of susceptibility measurements[1]. (At the Pd end of the series, the moments are found to be large, i.e., ~ 9-12 μ_B [Bohr magnetons]). Theoretical interpretations have emphasized the localized nature of these moments[1,2]. Recently reported Mössbauer measurements by Craig et.al.[3] on dilute solid solutions of Fe^{57} in Pd have confirmed the magnitude of the moment reported earlier[1] and have demonstrated that the moment associated with the Fe impurity acts, at low temperatures, like an isolated magnetic moment in an external magnetic field. However, for the cases of Fe in Rh and Fe in Mo, Craig et.al. find no hyperfine splitting due to a localized moment in apparent contradiction with the susceptibility experiments which give a moment of 2.2 and 2.1 μ_B respectively. The magnitude of the moment on the Fe atoms themselves has not been measured and hence the magnitude and spatial distribution of the magnetization of the localized states has not been determined.

This note is concerned with these aspects of the problem of the observed localized moments in metals. Starting with a basically simple idea, we show that measurements of the hyperfine field (e.g., by means of Mossbauer or NMR methods) can give this information - whereas susceptibility measurements cannot - and that the nature of the coupling between the spin on the Fe atom and the polarization of its surroundings can be inferred. In addition, the temperature dependence of the hyperfine field is derived and is shown to agree with experiment. However, in contrast with earlier work[3], our formulation emphasizes the explicit dependence of the hyperfine field H_{int} on the spin S' of the Fe atom and demonstrates why H_{int} versus temperature follows a Brillouin function of the total localized spin S(with S≠S').

We assume, as is generally done[4], that the internal field is proportional to the time average value of the z component of the spin on the Fe atom,

$$H_{int} = A \langle S'_z \rangle. \qquad (1)$$

This relationship is valid for the Fermi Hamiltonian for a free atom with L = 0 (in which case $A \propto |\psi(0)|^2$), and appears to hold, at least qualitatively, for a number of cases in metals and alloys.[4] While an exact visualization of the origin of A is not necessary, it is perhaps reasonable to assume that, for the case at hand, A arises mostly from the polarization of the s electrons in the core and conduction bands by the localized (3d) spin density on the iron atom. Since contributions to H_{int} from the polarized host atoms are also proportional to S' these may also be included in A.

For paramagnets, thermal relaxation times are so fast, relative to the γ-ray lifetime, that in the absence of an externally applied field H the average value of the spin $\langle S'_z \rangle$ is zero and hence no hyperfine splitting is observed in a Mössbauer measurement. When $H \neq 0$, one has the usual case of the alignment of the spins of the paramagnetic atoms and a thermal average of S'_z is given by,

$$\langle S'_z \rangle_T = S' B_{S'}(x). \qquad (2)$$

Here, $B_{S'}(x)$ is the Brillouin function for spin S', the parameter x is $g\mu_B S' H/kT$, and g is the gyromagnetic ratio (which we take to be 2 in what follows). For small x, i.e., large T or very small H, $B_{S'}(x)$ is given by $(S'+1)x/3S'$. The field at the nucleus, H_n, as a function of temperature is then,

$$H_n = H + H_{int} = H + A \langle S'_z \rangle_T = H + A\, S'\, B_{S'}(x). \qquad (3)$$

Since H is an additive constant, it is convenient to subtract H from the observed H_n and to discuss the remainder, i.e., H_{int}. (Since $H_n<0$ Craig et.al.[3] actually "added" H to H_n to obtain H_{int}.) For "ordinary" paramagnets, i.e., those for which the spin which gives rise to the hyperfine field and the spin which gives rise to the susceptibility are one and the same, Eq. 3 has previously been used successfully to explain[5] the observations[6] with the Mössbauer effect.

Consider now a spin S′ rigidly coupled to its polarized surroundings, the system forming a resultant spin S. (In general this coupling can be ferromagnet or anti-ferromagnetic in nature, but we shall assume in what follows that the coupling is ferromagnetic). Suppose we now take a collection of such spins S to form a paramagnetic system. In an external field, $\langle S_z \rangle_T$ is of course given by a Brillouin function for the spin S. Because of the rigid coupling, S′ "follows" S, and so $\langle S'_z \rangle_T$ is now given by,

$$\frac{\langle S'_z \rangle_T}{S'} = \frac{\langle S_z \rangle_T}{S} = B_S(x) \qquad (4)$$

instead of by Eq. 2, which holds only for a system of free spins S′ Therefore, we have that,

$$H_{int} = A \langle S'_z \rangle_T = A\, S'\, B_S(x) \qquad (5)$$

which, in the region of small x, is given by,

$$H_{int} = A\, S' \left[\frac{(S+1)}{3k}\, g\mu_B \frac{H}{T} \right]. \qquad (6)$$

Equations 5 and 6 display: (1) the physical origin of H_{int} through S′ and A and (2) the temperature dependence of H_{int} through the usual susceptibility

factor (which is concerned with the total spin S).

It follows from Eq. 5 that the saturation value of H_{int} is given by,

$$H_{sat} = A\,S' \tag{7}$$

and so we may therefore write,

$$\frac{H_{int}}{H_{sat}} = \frac{(S+1)}{3k}\, g\mu_B \frac{H}{T}. \tag{8}$$

Equation 8 is the phenomenological expression used by Craig el. al. to fit their data for Pd in the linear region and to determine S and hence μ. (They find that $\mu \approx 12.6\ \mu_B$ and $S \approx 13/2$.) Hence, we may take the agreement of our derived expression with experiment to indicate that our simple model is consistent with experience.

The above formulation allows us to determine S' provided we can obtain the value of A. Mössbauer measurements[7] at low temperatures (T=4°K) for Fe^{57} in a widely varying range of Co concentration (3 to 100%) in Co-Pd alloys give a value for A of $\approx$ -300 kgauss (which is also the value for Fe^{57} in metallic iron). Using this value of A as a reasonable approximation for the case of Fe^{57} in Pd and the observed H_{sat} value of -295 kgauss, we find that $S' \approx 1$ and $\mu \approx 2\ \mu_B$.

Equation 6 also allows us to reconcile the apparent contradiction between the Mössbauer and susceptibility measurements for Rh and Mo referred to earlier. This expression shows that although the total spin S may be large (as determined by susceptibility measurements), the hyperfine field will be small if S' is small. (Since A depends on environment[4] it will, in general, not have the same value as estimated above; this effect on H_{int} is probably smaller than the variation in S'.) We believe that the negative

Mössbauer results for these cases are attributable to a very small moment ($\mu < 0.3\mu_B$) on the iron atoms yielding an H_{int} which is unresolved in the range of $H/_T$ at which the measurements were made.

It is not yet clear how the induced moment, about 10.6 μ_B per Fe atom, is distributed among the Pd host atoms. Theoretical calculations are, of course, exceedingly difficult to do[2]. A much more likely approach is to do either NMR or Mössbauer measurements on the host nuclide, or neutron diffraction measurements on the less dilute (i.e., 1% Fe) alloys. The simplest and most naive model, which assumes a polarization of only the nearest-neighbor Pd atoms, gives a moment of approximately 0.9 μ_B and a spin of 1/2 per Pd atom. The inclusion of second nearest neighbors, which is more realistic, reduces the induced Pd moments to 0.5 μ_B per Pd atom. It is surprising that even this crude an estimate can yield a not too unreasonable result.

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